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ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL AND PHYSICAL CHEMISTRY

The experiment of diffusion by the three layer method. I. Sakurada and M. Taniguchi. *J. Soc. Chem. Ind. Japan*, **40**, 227-229 (1937).—Though the four layer method by means of the Öholm vessel has been generally applied to the expt. of diffusion on high molecular compds., the three layer method has been devised by the authors. In order to carry out the expt. of diffusion with less error the value of $h^2/(4Dt)$ should be selected near 0.16. (h denotes the height of layer by cm, D diffusion const. by cm^2/day , and t time measured by days). When the three layer method is taken for this expt. the normal diffusion const. can be obtained under the condition of $(4Dt)=0.36$, and t , the time of diffusion, is shortened more than half the time taken by the four layer method. The table of diffusion const. is given. The expt. carried out by the three layer method is compared with that by the four layer method with the sample of acetylcellulose dextrine. As the results of this comparison the three layer method is assured to be more applicable.

J. C. L.

Chemical study by molecular rays : Direct measurement of effective radius of reacting particles. I. Cl_2 and Na. S. Sasaki, E. Nishibori, and K. Uchida. *J. Chem. Soc. Japan*, **57**, 1277-1283 (1936).—By introducing atomic rays of Na from the lower part of gaseous Cl_2 and by illuminating them from the side with intensely white light, the sum of the effective radius for the reaction of $\text{Cl}_2 + \text{Na}$, $\sigma = r_{\text{Cl}_2} + r_{\text{Na}}$, was measured to be $\sigma = 3.53 \text{ \AA}$ by the method of searching for

fluorescence due to Na. When the above sum was calcd. on the basis of the classical gas theory, $\sigma = 3.60 \text{ \AA}$ was obtained. These two values were proved to be approximate.

II. Na and O_2 . S. Sasaki, E. Nishibori, G. Kondo and K. Kotera. *ibid.*, 1284-1290 (1936).—By introducing atomic rays into the tube in which N_2 or O_2 under various pressures ($10^{-5} \sim 10^{-3} \text{ mm}$) was enclosed and by putting them in collision with one another, the reacting radius was calcd. from the measured mean free path as follows: (1) $\sigma = 6.46 \times 10^{-8} \text{ cm}$, (2) $\sigma = 6.13 \times 10^{-8} \text{ cm}$, for O_2 ; $\sigma = 6.46 \times 10^{-8} \text{ cm}$ for N_2 . These show that there is little difference between the effective radius in $\text{Na} + \text{O}_2$ and that in $\text{Na} + \text{N}_2$.

III. I_2 and Na. E. Nishibori. *ibid.*, 1291-1299 (1936).—By giving atomic rays of Na at right angle to the molecular rays of I_2 or naphthalene, σ , the effective radius for I_2 —Na, and σ' , that for naphthalene—Na, were measured from the decrease in intensity of the molecular rays. The ratio obtained is $\sigma/\sigma' = 0.945$. From this result it was found that I_2 and Na react by approaching each other nearly to the extent of the collision assumed in the gas theory.

J. C. L.

Relation between the electron theory of metals of Sommerfeld and that of Frenkel. M. Satô. *Sci. Repts. Tôhoku Imp. Univ.*, **I**, 25, 1136-1140 (1937).—Assuming that the motion of a particle moving in Fermigas is a degenerated Brownian motion, the present writer derived Sommerfeld's electric and thermal conductivity of metals from Frenkel's electron theory.

Author.

A note on the mutual potential energy of two deuteron nuclei. K. Umeda, S. Tomonaga and Y. Ōno. *Sci. Papers Inst. Phys. Chem. Research*, **32**, 87-96 (1937).—Exchange energy and van der Waals energy of two deuteron nuclei are calcd., assuming the eigenfunction of deuteron to be dependent of the relative distance of proton and neutron as well as of the coordinate of the centre of mass, both in the Gaussian form. Majorana interaction between neutron and proton is taken in the Gaussian, the exponential or the rectangular hole form. If the centre of mass of each of both deuterons is very diffusely defined, a very strong attraction comes into play in the case of antiparallel spins, so that two deuterons in a nucleus show a tendency to amalgamate into an α particle, and in the case of the other spin orientations a strong repulsion will take place. If the centre of mass of each of both deuterons is very sharply defined, the van der Waals energy is much stronger than the exchange energy. The dependency of these forces on the relative distance between the two deuterons is not expressed in the δ -function, as claimed by Bethe and Bacher, but it is expressed in a Gaussian function, the decrement of which is found to be twice in amt. of that of the eigenfunction of deuteron. Authors.

A note on the overlapping integral. S. Tomonaga and K. Umeda. *Sci. Papers Inst. Phys. Chem. Research*, **32**, 97-102 (1937).—The allowable sharpness of locating the centre of mass of each of two atoms is deduced, on the condition that the overlapping integral of the two atoms is consistent with the Heitler-London's finite value calcd. for fixed nuclei: $2 \frac{M}{m+M} \frac{m}{m+M} \alpha \ll \text{linear dimension locating centre of mass} \ll \frac{M}{m+M} \alpha$, where m and M are the masses of electron and nucleus resp. and α is the radius of atom. The above equation explains the former result obtained in the previous paper, namely, the overlapping integral of two deuterons vanishes, also in the case where a perfect coincidence of their centres of mass takes place, if the

latter is strictly defined.

Authors.

On the dynamical liquid drop model of atomic nuclei. K. Umeda and Y. Ōno. *Sci. Papers Inst. Phys. Chem. Research*, **32**, 120-128 (1937).—Thomas-Fermi's liquid drop model of atomic nuclei is treated dynamically in the same way as Bloch has done for atomic electrons. Proper frequencies ν of the vibration of the liquid drop with l^{th} spherical harmonics are given by the roots of the known mathematical equation, $lJ_{l+\frac{1}{2}}(x) - xJ_{l-\frac{1}{2}}(x) = 0$, as $\nu = \frac{\sqrt{D}}{2\pi R} x$, where \sqrt{D} is a universal nuclear const. ($8.94 \cdot 10^{21} \cdot \left(\frac{e^2}{mc^2}\right) \cdot \text{sec}^{-1}$) and R the radius of nucleus. The frequencies are, accordingly, inversely proportional to the cubic root of the mass number. The lower frequencies have the same order of magnitude as that of γ -rays. Authors.

A note on the polymerisation of styrene as revealed by the Raman effect. S. Mizushima, Y. Morino and Y. Inoue. *Bull. Chem. Soc. Japan*, **12**, 132-135 (1937).—A polymer of styrene, prep'd. by heating the monomer $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ at 130°C for 10 hrs., for which the cryoscopic measurement (in benzene soln.) gave a molecular wt. of 1150 (polymerisation degree=11), showed the intensity ratio of the Raman lines 1634 cm^{-1} to 1602 cm^{-1} to be 1/10 times as large as that of the monomer. If the intensities of the lines 1634 and 1602 are proportional to the number of ethylene bonds and benzene nuclei, resp., the observed intensity change conforms with the view that polystyrene is not cyclic, but consists of thread molecules. The polymerisation process is also studied at room temp. by means of such an intensity measurement.

Authors.

Polarization-interference-fringe in Hilger E₁ quartz spectrograph. H. Yoshinaga. *Japan. J. Phys.*, **12**, 1-7 (1937).—In order to explain the interference fringe and its disappearing point which appear in such a quartz spectrograph as Hilger E₁ type for polarized continuous light, the intensity of the

light falling into the photographic plate was calcd. when the plane polarized light, the plane of polarization of which had the inclination of 45° to the direction of the slit of the spectrograph, was used. This light becomes in general the elliptic polarized light for the interference effect in the total reflection prism (the phase difference of the ordinary and extraordinary light: φ). The deformation of the ellipse expressing locus of this elliptic polarized light in consequence of the rotation of the plane of polarization in the lens, the 30° prism (θ and ρ resp.), the unequal reflection at the surface of the 30° prism and the photographic plate (this value being calcd. by Fresnel's equation) was calcd. and the intensity I of the light in the photographic plate was obtained in such a relation as $I = f_1(\theta, \rho) + f_2(\theta, \rho) \cos \varphi$. The other method to obtain $f_2(\theta, \rho)$ is also shown. It is found in this relation that the interference fringe appears for the variation of the value of φ corresponding to various wave lengths and the disappearing point of the fringe is obtained from the condition of $f_2(\theta, \rho) = 0$. This condition explains the change of θ corresponding to the light, for which the disappearing point of the fringe appears, from both of the even and odd multiples of $\frac{\pi}{2}$ (the latter case being newly observed by the author), particularly in the short wave length side. The value of the change of θ calcd. in such a way coincides well with the exptl. value.

Author.

Studies on solubilities. III. On the solubilities of isomers. 3. S. Sugito. *Tech. Repts. Kyushu Imp. Univ.*, 12, 62-78 (1937).—The solubilities of benzoic acid (A), O-, M-, P-oxybenzoic acid (B, C, D), O-, M-nitrobenzoic acid (E, F) in dry benzene (I) and in wet benzene (II) contg. 0.058% water which was prepared by saturating the benzene with water at 23.00°C . were detd. between 20° and 80°C . by synthetic method with extremely dry solutes and solvents. The exptl. data were as follows: C indicates the solubility in wt. per cent. at 1°C .

- (A) (I), $\log C = +0.550552 + 0.0202192 t$
 $-0.0000665412 t^2$
 (II), $\log C = +0.566025 + 0.0200100 t$
 $-0.0000668710 t^2$
 (B) (I), $\log C = -0.625606 + 0.0205078 t$
 $-0.000000962401 t^2$
 (II), $\log C = -0.563052 + 0.0201277 t$
 $-0.00000682281 t^2$
 (C) (I), $\log C = -2.740276 + 0.0227176 t$
 $+0.0000153119 t^2$
 (II), $\log C = -2.44720 + 0.0154237 t$
 $+0.0000713674 t^2$
 (D) (I), $\log C = -2.80681 + 0.0232968 t$
 $-0.0000231507 t^2$
 (II), $\log C = -2.71287 + 0.0223777 t$
 $-0.0000176123 t^2$
 (E) (I), $\log C = -1.046880 + 0.0195520 t$
 $+0.0000285595 t^2$
 (II), $\log C = -0.86759 + 0.0157978 t$
 $+0.0000518276 t^2$
 (F) (I), $\log C = -0.245776 + 0.0194305 t$
 $-0.00000339524 t^2$
 (II), $\log C = -0.085387 + 0.0143745 t$
 $+0.0000370574 t^2$
 Author.

Boundary layer profiles made visible by means of Wilson photograph of alpha rays. M. Matukawa. *Proc. Imp. Acad. (Tokyo)*, 13, 98-100 (1937).—A new method of directly photographing the velocity distribution curves in the air flow was invented and applied to the boundary layer investigation. It consists of C.T.R. Wilson's method of photographing the ionisation tracks of α -rays emitted normally through the boundary layer of a moving object. Owing to the air flow caused by the motion the tracks suffer some distortion which reveals in a striking and concrete manner the velocity profiles.

Author.

K-absorption spectra of copper. T. Hayashi. *Sci. Repts. Tohoku Imp. Univ.*, 25, 661-685 (1936).—Using a focussing X-ray spectrograph of Cauchois type, the K-absorption spectra of copper in the states of Cu metal, Cu-Ni alloy, α -brass, β -brass, Cu_2O , CuO , CuSO_4NH_3 and CaCO_3 are observed.

(1) Pure Cu shows three steps in the K-absorption edge: the longest wave-length edge K_1 , the shortest K_2 and a faint edge K' . These are due to the electron-jumps $K-M_{IV}$, $K-N_I$, $K-N_{IIIII}$ resp. In the alloy Ni-Cu and α -brass, the Cu-K-absorption edge is similar to that of pure Cu. The edge K_1 has the same wave length as in pure Cu. (2) An edge near the position K_2 alone appears in $CuCO_3$ and $CuSO_4 \cdot NH_3$. In Cu_2O the edges are very similar to those in pure Cu, except that a new faint edge K'' appears on the short wave-length side of K_2 . In CuO occurs a three-step edge, shorter in wave-length than those in Cu_2O , but longer in wave-length than those in $CuCO_3$ and $CuSO_4 \cdot NH_3$. The observation shows no direct correlation with the valence of the Cu-atom. (3) In β -brass, which is an inter-metallic compd., there is one edge near K_1 in pure Cu. It accompanies a very fine substructure on the short wave-length side. (4) Fine-structures occurring in the region of wave-lengths shorter than the principal edge of Ni and Cu in pure Cu, pure Ni, Ni-Cu and α -brass, which crystallise all in face-centered cubic lattices, are all similar. The fine-structure of Ni absorption spectrum in Ni-Cu shows the same energy-seps. as that of Cu in the same alloy. Author.

Densities of tungsten filaments. R. Tajime. *Mazda Kenkyu Jiho*, 12, 51 (1937).—Ten years ago, when the author reported the results obtained by the direct measurement, they did not agree with the values computed by the structural data adopted generally at that time. It is of interest to notice that the recently published data detd. by X-ray analysis have come to coincide sensibly with the author's direct measurement $\rho = 19.27 (\pm 0.01)$ for well aged pure filaments ranging from 80μ to 14μ in diameter and $\rho = 19.26$ for a single crystal. The mean value for 1% thoriated aged filaments is $\rho = 19.07 (\pm 0.02)$. These densities are independent of diameters within the range. For unaged wires the densities decrease about 0.7% as the drawing proceeds from 40μ down to 14μ for the both kinds. No change in length

exceeding the exptl. error ($\pm 0.01\%$) was observed by the aging of these drawn wires.

Author.

Kokutai-Ondo (Black body temperature). R. Tajime. *Mazda Kenkyu Jiho*, 12, 50-51 (1937).—The Japanese term "Kokutai-Ondo" is the translation of the German "schwarze Temperatur". Since the high temp. measurement developed most precisely in America 20 years ago, the black body temps. have been classified into three kinds, namely, "brightness temp.", "color temp." and "radiation temp." In Japan, though this classification in terminology is most widely adopted by illuminating and radio engineers, some physicists and almost all of metallurgists still now follow the inadequate term "schwarze Temperatur", not improved in Germany and in Holland (zwarte temperatuur). It seems to be better to follow the American classification, in which the term "black body temp." has now no physical significance, unless the kind of black body temp. is assigned, e.g. "black body brightness temp."

Author.

Measurement of circular dichroism in the ultra-violet regions. I. R. Tsuchida. *Bull. Chem. Soc. Japan*, 12, 276-285 (1937).—The author has proposed an accurate modified method of Kuhn and Braun for measuring circular dichroism and worked out a general equation for the measurement. $\epsilon_r - \epsilon_l = \frac{2}{cd} \arcsin h (\tan 2\tau \cos 2\omega)$, where τ and ω are variables representing angular positions of the polarizer and the analyser of the optical system, while ϵ_r and ϵ_l are the extinction coeffs. for right and left circularly polarised rays. The range of applicability is discussed for the approximate equation, $\epsilon_r - \epsilon_l = \frac{5}{cd} \tan 2\tau \cos 2\omega$. The circular dichroism as well as the rotatory dispersion of α -bromocamphor- π -sulphonate were measured in the visible and the ultra-violet regions. Author.

Rhythmic precipitates. VIII. On the rhythmic precipitates of lead iodate

in gelatine gel. T. Isemura. *J. Chem. Soc. Japan*, 58, 301-304 (1937).—The formation of rhythmic ppts. of lead iodate by the diffusion of acetate or nitrate of lead into the gelatine jelly contg. potassium iodate is reported. In ordinary commercial gelatine which always contains some impurities of chlorides and phosphates, the rhythmic bands of lead iodate becomes undistinguishable by a strip of white ppts., probably consisting of chloride and phosphate of lead. With gelatine purified by electro-dialysis or Loeb's method, very beautiful and well defined rhythmic ppts. are formed. Lead iodate makes often the helicoidal ppts. The reason for the formation of these ppts. is not thoroughly clear. The effects of the concns. of outer- and inner-electrolyte and gelatine jelly were investigated. The increase of the concn. of outer- and inner-electrolyte makes the intervals of bands closer, and the number of bands formed is increased, but the increase of the concn. of gelatine makes the distance between bands larger, and the number of bands formed diminishes. Light has no influence. The higher the temp. is, the smaller the number of bands and the larger the intervals between bands. Author.

On Gerlach's thermomagnetic-electromotive force in nickel, iron and nickel-iron alloys. N. Yamanaka. *Sci. Repts. Tohoku Imp. Univ.*, 26, 40-47 (1937).—Gerlach's thermomagnetic e.m.f. generated in nickel, iron and seven kinds of nickel-iron alloys was studied. The main results obtained are: (1) the behaviours in the magnetic field and also under the temp. gradient are similar to the results already reported for nickel and some ferromagnetic alloys; (2) the max. satn. value of this e.m.f. is the greatest in nickel and the least in 35% Ni-Fe alloy; (3) in iron, the e.m.f. shows the inversion of its sense in some strength of the magnetic field in the cold drawn specimen as well as in the specimen re-crystallised by annealing. Author.

On the ultra-sonic and chemical reactions. II. Effects on fats and

oils. T. Tazuhama. *J. Electrochem. Assoc. Japan*, 5, 225-228 (1937).—This report is the descriptions of the chem. effects of ultra-sonic radiations on fats and oils compared with those of mech. agitations (600 R/min) at the same temp. The oils used were soyabean, liver, sardine, whale and shark oils. The oscillator was 250 watts push-pull with vibrator of crystal, the frequency being 500 kc/sec. This produced oil spurts about 10-15 cm high. The effects of ultra-sonic and heat-agitation were small in vegetable oils. Marked effect was observed in fish oils decreasing the I.V. and increasing the S.V., A.V., refractive index and sp.gr., and the action was greater in the case of ultra-sonic waves than in the case of heat-agitations. The change of oils seems to be due to the oxidation, polymerization and decompn. The addn. of active carbon or Japanese acid clay accelerated the change of oils under ultra-sonic radiations, distinct deodorization and decolorization was observed. It was recognized that the ultra-sonic radiations increase the drying property of oils. For this change it seems that the oxygen in the air plays important action. Author.

On the crystal structure of thiophosphoryl bromide PSBr_3 . I. Nitta and K. Suenaga. *Sci. Papers Inst. Phys. Chem. Research*, 31, 121-124 (1937).—The X-ray crystal structure of PSBr_3 was investigated. The crystal is cubic with $a=11.03 \text{ \AA}$, $Z=8$, space group T_h^6-Pa3 . The density measured is $d_{\text{obs}}=2.97$ ($d_{\text{calc}}=2.99$ from X-ray data). The structure as given is probably quite similar to that of SnJ_4 , with P and S on the trigonal axes, Br in general positions, and min. molecular symmetry of C_3-3 . Intermolecular forces and the possible existence of double molecules are discussed. Authors.

On the effects of stress on Gerlach's electromotive force in nickel, iron, and nickel-iron alloys. N. Yamanaka. *Sci. Repts. Tohoku Imp. Univ.*, 26, 48-54 (1937).—The effects of tension and torsion on Gerlach's thermomagnetic e.m.f. generated in nickel, iron and nickel-iron alloys are summarised as

follows. (1) In nickel, and nickel-iron alloy (87.5% Ni), the satn. value of the electromotive force and the intensity of magnetic field at which the electromotive force is satd. increase with increase of tension. (2) In nickel-iron alloys which contain less than 87.5 per cent. of nickel, the greater the tension applied, the smaller the electromotive force generates. (3) In iron, the application of tension results on the one hand in diminution of the pos. max. value of the electromotive force, and on the other hand in displacement of the field intensity, at which the electromotive force changes its sign, toward the weaker field. (4) The torsion causes the decrease of the electromotive force in iron and nickel.

Author.

Rhythmic precipitates. IX. On the rhythmic precipitates of silver carbonate, silver iodate, and silver arsenite in gelatine gel. T. Isemura. *J. Chem. Soc. Japan*, 58, 629-637 (1937).—The conditions for the formation of rhythmic bands of silver carbonate, silver iodate, and silver arsenite in gelatine jelly were investigated. These salts form well-defined rhythmic band in ash-free gelatine which is made by Loeb's method. But in ordinary non-dialysed commercial gelatine which always contains phosphates and chlorides, the bands of above mentioned silver salts become undistinguishable from the ppts. of silver phosphate and chloride, just as the lead iodate bands became undistinguishable from lead phosphate and chloride, as already pointed out in the previous communication. The effects increasing the concns. of inner- and outer-electrolytes and gelatine jelly and the influence of temp. on the formation of rhythmic bands and on the intervals between bands were studied. The effects of concns. are parallel to those in the case of lead iodate. In the case of silver iodate and silver arsenite, the higher the temp. is, the smaller the number of bands becomes, and the larger the intervals are. In the case of silver carbonate, however, the higher the temp. is, the smaller the intervals are. The effects of interchange of inner- and outer-electrolytes were also investi-

gated. In general, no influence on the formation of rhythmic bands is observed when the excess of diffusing outer-electrolyte does not make a soluble complex salt of the salt which makes the rhythmic bands. Author.

Studies on the flow of gaseous mixtures through capillaries. I. The viscosity of binary gaseous mixtures. H. Adzumi. *Bull. Chem. Soc. Japan*, 12, 199-226 (1937).—Viscosities of the following six simple gases and seven binary gaseous mixts. were measured by the transpiration method at the temp. range $20^{\circ}\sim 100^{\circ}\text{C}$: H_2 , CH_4 , C_2H_2 , C_3H_8 , H_2CH_4 , $\text{H}_2\text{C}_2\text{H}_2$, $\text{H}_2\text{C}_3\text{H}_8$, $\text{H}_2\text{C}_3\text{H}_6$, $\text{H}_2\text{C}_3\text{H}_4$, $\text{C}_2\text{H}_2\text{C}_3\text{H}_8$, $\text{C}_2\text{H}_2\text{C}_3\text{H}_6$, and $\text{C}_3\text{H}_8\text{C}_3\text{H}_8$. The viscosities of the first four mixts. attain max. values at definite compns., which are about 20% of H_2 for the mixt. H_2CH_4 and about 70-80% of H_2 for the other three. Of several formula proposed to express the viscosity of gaseous mixts., the formula in which Kuenen's consideration of the persistence of molecular velocity is introduced seems to be the most appropriate. The results of observation can be expressed satisfactorily by that formula, if we take a proper value for one of Sutherland's consts., which is due to the attraction between the different molecules and can not be detd. directly. The theoretical consideration of this Sutherland's const. by Schmick and London was examd. by thirty-two examples. The conditions for the occurrence of a max. and a min. points were obtained from the discussion of the viscosity formula examd. numerically for fifty-five mixts., and found to be always correct except for only five cases. The viscosity-compn. curve deviated in general from a straight line. The deviation depends on the ratios of molecular wts., molecular diameter, and Sutherland's consts. of two component gases. Especially the max. point is very liable to occur if the ratio of two molecular wts. is great. It has been shown that, if the persistence of molecular velocity be neglected, the condition for the occurrence of a max. point cannot be fulfilled and the consideration of the persistence is absolutely necessary to ex-

plain this point. The compn. of the max. point changes with the change of temp. This is found to be due to the difference of Sutherland's consts. of two component gases. The mean free path of each component gas was calcul.

II. The molecular flow of gaseous mixtures. *ibid.*, 285-291 (1937).—The quantities of the following simple gases and gaseous mixts. flowing through the capillary at very low pressure were measured: H_2 , C_2H_2 , C_3H_6 , $H_2 \sim C_2H_2$, and $H_2 \sim C_3H_6$. The rates of the molecular flow of simple gases are expressed satisfactorily by Knudsen's formula. The rates of molecular flow of mixts. are considered to be additive of the components. This consideration was confirmed by the measurements of the quantities of flow of mixts. The changes of the compn. of the mixts. after flowing through the capillary at low pressures were measured and the results show also the validity of the additivity law.

III. The flow of gaseous mixtures at medium pressures. *ibid.*, 292-303 (1937).—The quantities of the following seven simple gases and six gaseous mixts. flowing through the capillary were measured at the pressures between 4 and 0.01 mm: H_2 , C_2H_2 , C_3H_6 , $H_2 \sim C_2H_2$, $H_2 \sim C_3H_6$; C_6H_6 , CCl_4 , $CHCl_3$, $(C_2H_5)_2O$, $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, $(C_2H_5)_2O \sim CHCl_3$. The quantity of flow, K , is a function of the mean pressure, p , and the K - p curve passes through a min. point. The occurrence of a min. point of mixts. is more remarkable than that in the case of simple gases. The quantities of flow of simple gases are satisfactorily expressed by $K = ap + \gamma b$, where γ is a coeff. which becomes a const. at higher pressures ($=0.9$) or at very low pressures ($=1.0$), and varies from 0.9 to 1.0 at

the intermediate conditions. The quantities of flow of mixts. are also expressed by a formula analogous to that of simple gases. The values of γ' at higher pressures of the mixts. are const. for varying compns. of the same combination of components, but different from those for different combinations and simple gases. These values are also considered to be dependent of the chem. configurations of two components. The viscosities of the following mixts. are calcul. from the quantities of flow: $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, and $(C_2H_5)_2O \sim CHCl_3$. The mixt. $CCl_4 \sim CHCl_3$ shows a max. at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight.

J. C. L.

On the flow of gases through a porous wall. H. Adzumi. *Bull. Chem. Soc. Japan*, 12, 304-312 (1937).—A formula for the flow of a gas through a porous plate is derived and it is found that the observed quantity of flow is satisfactorily expressed by the formula. The method of estimating the values of the mean radius and the number of pores of a porous plate is proposed.

J. C. L.

The decomposition of methane on the surface of platinum. I. II. M. Kubokawa. *This Journal*, 11, 82-106 (1937).

The kinetics of the catalytic hydrogenation of ethylene with nickel. I. O. Toyama. *This Journal*, 11, 153-165 (1937).

A note on "The decomposition of methane on the surface of platinum." M. Kubokawa. *This Journal*, 11, 217-219 (1937).

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

On the electron theory of metal. K. Ariyama. *Sci. Papers Phys. Chem. Research*, 32, 103-119 (1937).—Ferromagnet-

ism is explained with calcul. by means of an electron model used and a polar model of metal atom proposed by Schubin—

Wonsowsky in 1934-35 in order to elucidate at the same time the electric and magnetic properties of metal. The theory is improved with the primary combination of plane wave instead of single wave. It is assumed that the number of polar atoms is less than that of the whole atoms, and the conditions under which metal should show its ferromagnetism at lower temp. are deduced. As for the intensity of satd. magnetism, a factor proportional to $T^{3/2}C^{1/2}/T$ is added besides a factor proportional to $T^{3/2}$. J. C. L.

On the binding energy of atomic nuclei. I. II. T. Yamanouchi. *Proc. Phys.-Math. Soc. Japan*, III, 19, 557-565; 790-797, (1937).—The eigenfunction of an atomic nucleus is assumed to be approximated by suitably symmetrised product of eigenfunctions ψ of constituent particles. ψ is supposed to have no spatial degeneration, which simplifies the energy expression compared to the central field approximation. The forces between particles are assumed to be all equal, and the mass defects of the nucleus of the mass number $4p+n$ ($n=1, \dots, 4$) are expressed as the quadratic function of n , which is shown to be in good accord with the observed values for $p=2, \dots, 9$ for the stable nuclei. Regarding proton and neutron as inequiv. ψ is taken different for these two kinds of particles, and it is shown that the mass defects of 6 nuclei between N^{13} and N^{16} are correct within the exptl. error. It follows from these calcns. that the forces between like particles are smaller than that between unlike particles. And the effect of the difference of ψ of proton and neutron on the successive construction of nuclei is discussed. Author.

High speed photography using the explosion of wires. T. Kano. *Mazda Kenkyu Jiho*, 12, 43-45 (1937).—There are many reports about the intense flash light arising from the explosion of wires. Dr. Nagaoka reported the character of the spectrums of this flash lights and Dr. Suehiro used this light for photography. This paper describes the new method of high speed photography

by using Ignitron or Thyatron to catch the proper instant of the phenomena in this kind of photography. Author.

On the redetermination of the elementary charge by the oil drop method.

Y. Ishida, I. Fukushima and T. Suetsugu. *Sci. Papers Inst. Phys. Chem. Research*, 32, 57-77 (1937).—"e" as one of the phys. consts. was investigated by the oil drop method with special attention on the following points.

1. The effect of the convection current on the speed of the oil drop.
2. The evaporation and oxidation (or adsorption) of the oil drop.
3. The effect of the arc on the oil drop.
4. The shape of the oil drop.

Besides due precautions were taken on the potential and the temp. The main difficulties in the oil drop method seem to have been heretofore, first, in the use of the predetd. density of the oil drop under observation, and, secondly, in the use of non-spherical drops which are not permissible under Stoke's law in conjunction with spherical drops. Further, the effects of the convection current and the radiation from the arc appear to have some significance. Our detn. gives $e = (4.806 \pm 0.003) \times 10^{-10}$ e.s.u., using Harrington's value of the viscosity of air. The above probable error was obtained by taking the square root of the sum of the squares of all probable error coming in from the different factors used except that of the viscosity. If Kellstrom's detn. of the value of the viscosity of air is correct, then we come to the unavoidable conclusion that the electronic charge must be greater than the value detd. by the X-ray method. Authors.

On the transition effect by the absorption of γ -rays. T. Takeuchi and T. Sugita. *Bull. Tokyo Univ. Eng.*, 6, 391-395 (1937).—The transition effect of γ -rays of radium for different materials was detd. and explained by secondary ray. Authors.

Photographic demonstration of electronpair generation. T. Takeuchi and T.

Sugita. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 555-556 (1937).—A well-collimated beam of γ -rays from 10 mg of Ra filtered through 0.6 cm of Pb foil is used for generating electron-pairs in a Pb, Ag, Bi or Sn foil 0.02 cm thick. On emerging from the collimator of length 10 cm, rays pass through the generating element and the created electrons enter the region between two large circular poles of an electromagnet of Nagaoka's type. The paths of the electrons are bent into circles, the pos. electrons being bent one way and the neg. ones the other way. The electrons hit on an X-ray film of double emulsion in a Debye-Scherrer-Hull camera of radius of 6.25 cm. After 60 hrs. exposure, the distribution of density of blackening is measured with a microphotometer. There are found certain bands in the back-ground, but they are too faint to show in the reproduction. We should expect that kinetic energy is shared between an electron and its partner in different extent by different pairs, but none can attain a kinetic energy greater than $h\nu - 2m_0c^2 = h\nu - 1.02\text{MEV}$, where ordinary notations are used, so that there occur 5 upper cut-offs to the density of blackening. The K.E.'s can be detd. by the following relativistic formula

$$eV = 5.11 \times 10^5 \left\{ \sqrt{1 + \frac{(H\rho)^2}{2.19 \times 10^6}} - 1 \right\},$$

H the magnetic field being 1,600 oersteds and ρ being radius of curvature of track in cm.

Authors.

On the theory of collision of neutrons with deuterons. H. Yukawa and S. Sakata. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 542-551 (1937).—The problem of the neutron-deuteron collision was reduced to a simple form by taking the structures of the ^2H and ^3H into account and neglecting the forces depending explicitly on the spin. The form of the effective potential hole was detd. by comparing the estimated value of the cross section of scattering of slow neutrons by deuterons with that obtained experimentally. The cross section of capture was found to be small in agreement with the expt. The energy dependence of the scattering cross section is

also discussed. The theory of Fermi concerning the effect of the chem. binding on the scattering of slow neutrons was extended to more general case and a necessary limitation of the theory is discussed. The cross section for thermal neutrons was found to be nearly twice as large as that for neutrons of several volts. Theoretical reasons for the small contribution of the deuteron to the slowing down are considered. Authors.

Ternary system: $(\text{NH}_4)_2\text{SO}_4$ — $\text{Al}_2(\text{SO}_4)_3$ — H_2O . S. Uno. *Waseda Applied Chem. Soc. Bull. (Japan)*, **14**, (3) 18-20 (1937).—Solubility measurements were made for the ternary system: $(\text{NH}_4)_2\text{SO}_4$ — $\text{Al}_2(\text{SO}_4)_3$ — H_2O at 0°C , and the comps. of the satd. solns. with both $(\text{NH}_4)_2\text{SO}_4$ and NH_4 -alum at 0° , 20° , 30° , and 40°C were detd. The results are shown as follows: Table I. System $(\text{NH}_4)_2\text{SO}_4$ — $\text{Al}_2(\text{SO}_4)_3$ — H_2O at 0°C .

Compn. of satd. soln. by wt. %		
$(\text{NH}_4)_2\text{SO}_4$	$\text{Al}_2(\text{SO}_4)_3$	H_2O
41.56%	0%	58.41%
41.42	0.082	58.50
35.20	0.130	64.97
24.86	0.201	74.96
15.61	0.254	84.14
10.07	0.323	89.61
5.42	0.411	94.17
3.29	0.463	96.25
1.68	1.07	97.35
0.987	1.52	97.49
0.595	2.23	97.27

Table II. Satd. Points with both $(\text{NH}_4)_2\text{SO}_4$ and NH_4 -alum.

Temp.	Compn. by wt. %		
	$(\text{NH}_4)_2\text{SO}_4$	$\text{Al}_2(\text{SO}_4)_3$	H_2O
0°C	41.42%	0.082%	58.50%
20	42.72	0.359	56.93
30	43.30	0.654	56.05
40	44.08	1.37	54.55

Author.

Spectrochemical studies on the aqueous solutions of some chromic salts. H. Sueda. *Bull. Tokyo Univ. Eng.*, **6**, 333-350 (1937).—The absorption spectra of

various chromic chloride and sulphate hydrate solns. were quantitatively measured in the ultra-violet regions. The substitution of a chlorine atom for a water molecule in the aquo-chloro salts caused the absorption band to shift in the direction of increasing wave length and absorption capacity. For the modified green chromic sulphate, the formula μ -ol-mono or di-sulphato-di-chromic sulphate was reduced from its absorption spectra and the quantities of liberated sulphuric acid and sulphate ions which were pptd. by barium chloride in various dilns. The compd. obtained by heating for two or three minutes the hydroxo-pentaquo-chromic chloride soln. was considered as di-ol-octaquo-di-chromic chloride. The modification of the green chromic sulphate in aqueous soln. is discussed.

Author.

A note on the absorption of slow neutrons. S. Kikuchi, E. Takeda and J. Ito. *Proc. Phys.-Math. Soc. Japan*, III, 19, 43-52 (1937).—This expt. was made to confirm the assumption that the γ -rays emitted from matters by the bombardment of slow neutrons is due to the capture of neutrons. The cross section for exciting γ -rays was compared relatively with that for producing radioactive elements. There are only seven of these elements—Al, V, Mn, Co, Cl, Ni and Cu—for in other cases there occurs a kind of capture process by which a stable isotope changes into another stable isotope of mass one unit higher than the initial one. To obtain the relative cross section for producing radioactive element the absorption of β -rays was corrected in each case. The comparison of the results with the values for γ -rays excitation showed that the assumption in question is reasonable except the case of Cobalt. This may be due to the existence of other stable isotope of Co. The number of radioactive atoms produced in a certain substance when it is bombarded for sufficient length of time is compared with the number of quanta γ -rays emitted from the same substance during the bombardment. Considering the relation between the efficiency of the counter and the

energy of γ -rays, the result was reconcilable with the view that the emission of γ -rays and the production of radioactive elements belong to the same nuclear process.

Authors.

The OH-vibration spectrum in the photographic infra red. S. Mizushima, Y. Uehara and Y. Morino. *Bull. Chem. Soc. Japan*, 12, 132-135 (1937).—The OH vibrational absorption spectra were studied in the region of $9590 \sim 10,000 \text{ \AA}$ as well as $7300 \sim 7700 \text{ \AA}$. The compds. studied are CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$, $n\text{-C}_4\text{H}_9\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$, $p\text{-C}_6\text{H}_4\text{ClOH}$, $o\text{-C}_6\text{H}_4\text{ClOH}$, $o\text{-C}_6\text{H}_4\text{BrOH}$, and $o\text{-C}_6\text{H}_4\text{CH}_3\text{OH}$ for solns. in CCl_4 of 0.5 mol. The data are interpreted as the 2nd and the 3rd overtones of the OH fundamental. The frequency of infinitesimal vibration, the anharmonicity factor, and the disson. energy are calcd. from these values. The calcd. values of the first overtones are in fairly good agreement with those by Wulf and Liddel. Two frequencies are observed for the ortho-halogenated phenols, which confirm Pauling's suggestion that these compds. have two stereoisomers according to the quant. mech. resonance.

Authors.

Theory of sl-triplet of alkaline earth. G. Araki. *Proc. Phys.-Math. Soc. Japan*, 19, 592-608 (1937).—The theory of the fine structure of helium recently worked out by the author is extended to the case of alkaline earth. The general expressions for sl-triplets and singlets are derived, taking into account the spin-orbit and spin-spin interactions between all electrons. The numerical calcs. for $1s^2 2s 2p \text{ } ^3\text{P}$, $1s^2 2s 3d \text{ } ^3\text{D}$, and $1s^2 2s 4f \text{ } ^3\text{F}$ of Be, B^+ , C^{++} , N^{+++} , and O^{++++} are carried out. The calcd. values are in good agreement with the exptl. data. The departure of the interval ratios of triplet levels from the Landé rule are quantitatively explained on a purely theoretical stand-point.

Author.

Researches on the concentration of hydrogen ions contained in the aqueous solutions of complex cobaltamines and their absorption spectra. IV. A-

aqueous solutions containing oxalato-radical. T. Uemura and N. Hirasawa. *Bull. Tokyo Univ. Eng.*, 6, 278-286 (1937).—The present studies are a continuation of the researches already reported by the authors. All the salts treated in this paper contain the oxalato (C_2O_4) radical in their complex nucleus. Of the seven samples taken, the two salts, $[Co(C_2O_4)_2(H_2O)OH]K_2$ and $[Co(C_2O_4)(NH_3)_5]Cl \cdot HCl$, did not show any selective absorption in their ultra-violet region. The other five complex salts which have their selective absorption in ultra-violet parts are not greatly influenced by the variation of hydrogen ion concn. (pH). When the number of oxalato-radical is increased in its complex radical, the wave length given by the centre of max. absorption is shifted to a longer side. Aqueous solns. of complex salts get their pH-values increased by the insertion of ammonia molecules; the soln. becomes more alkaline with the increase of ammonia molecules in complex nucleus. The list of the samples which have been prepd. for the study is as follows:

- (1) $[Co(C_2O_4)_3]K_3 \cdot H_2O$,
- (2) $[Co(C_2O_4)_2(H_2O)OH]K_2$,
- (3) $[Co(C_2O_4)_2(NH_3)_2]K \cdot H_2O$,
- (4) $[Co(C_2O_4)(NH_3)_2(NO_2)_2]K \cdot H_2O$,
- (5) $[Co(C_2O_4)(NH_3)_3(H_2O)]Cl$,
- (6) $[Co(C_2O_4)(NH_3)_4]Cl$,
- (7) $[Co(C_2O_4)(NH_3)_5]Cl \cdot HCl$.

Authors.

Stark effect of ionized helium. Y. Ishida, S. Hiyama and H. Kubota. *Sci. Papers Inst. Phys. Chem. Research*, 31, 265-280 (1937).—The Stark effect is measured of ionised helium excited in lo-Surdo quartz tubes for the first, the second and the third members of the series, i.e., $\lambda\lambda$ 4685, 3203 and 2733 Å resp., the first up to 600 KV/cm, the second and the third up to 300 KV/cm. It was found that the exptl. data coincided quite well with those of the displacements and intensities calcd. from the wave mech. theory of Schroendinger.

Authors.

The third absorption band of co-

ordination compounds. II. Configuration of $[Co(NH_3)_3(NO_2)_2Cl]$ and $[Co(NH_3)_3(NO_2)_2Br]$. M. Kobayashi, A. Hagitani and I. Mita. *J. Chem. Soc. Japan*, 58, 391-392 (1937).—Y. Shibata has concluded that the third absorption band of the nitro-ammine cobaltic compds. is due to the nitro-radicals co-ordinated in trans-position to each other. The authors, therefore, measured the extinction coeffs. of $[Co(NH_3)_3(NO_2)_2Cl]$ and $[Co(NH_3)_3(NO_2)_2Br]$, and found the corresponding third band for each. It was concluded that in these two complexes the two nitro-radicals are co-ordinated in trans-position to each other.

Authors.

Spectrographic methods of studying unstable compounds. III. Influence of KBr on rotatory dispersion of d- $[Co en_3]Br_3$ in aqueous solution. R. Tsuchida. *J. Chem. Soc. Japan*, 58, 621-628 (1937).—The author has found that the optical rotation of d- $[Co en_3]Br_3$ in aqueous soln. is markedly increased by addn. of KBr. Rotatory dispersion of a set of mixed solns. of the active complex salt and potassium bromide was investigated in the ultra-violet as well as the visible regions. Thus the increase in optical rotation was concluded to be due to the formation of an unstable complex radical [d- $[Co en_3]Br_3$]. The author also referred to the structure of 'two-shelled complex compds.'

Author.

Excitation of gamma rays by fast neutrons. H. Aoki. *Proc. Phys.-Math. Soc. Japan*, III, 19, 557-565 (1937).—Relative cross sections of 41 elements for gamma rays excitation by neutrons of 2.4 m.e.v. energy were detd. Plotted against the atomic number of elements, they distribute near a smooth curve which rises with atomic number in the region of lower atomic number and probably falls again at the heaviest stable-elements. The energies of the gamma rays were detd. in 11 elements by the method of coincidence of two thin walled Geiger-Müller counters. The absorption curves of the secondary electrons were different in each element, showing

that the spectra of gamma rays are different. But no gamma rays were observed whose energies exceed 2.4 m.e.v. Thus, it is very probable that the gamma rays are phosphorescence gamma rays excited by neutrons. The cross sections for the excitation of gamma rays are compared with those for absorption of neutrons and also for the production of slow neutrons by the passage of neutrons through the matter.

Author.

Paschen series of hydrogen and deuterium. II. Nagaoka and T. Mishima. *Proc. Imp. Acad. (Tokyo)*, **13**, 95-97 (1937).

—A 30 KW transformer was operated by 50 A. a. c. at 200 V, 50~, and the current from the transformer led to a condenser of 0.003 μF capacity, and to the electrodes, which consisted of spheres of 10 cm radius, made of Cu-sheets, with the spark gap of 2.5 cm. The discharge tube (15 cm diam., 100 cm long) was made of terex glass, and one end was closed with a thick plate of silica glass. Hydrogen was prepd. by electrolysis of water, and deuterium from heavy water of 99.5 per cent purity. As the adjustment of pressure formed the most delicate part of the expt., special needle valve was introduced to electrodeless discharge. The gases were excited under pressure of 0.025 to 0.03 mm. The optimum pressure may vary with the width of the tube and the discharge current. Steinheil spectroscope with three flint glass prisms was used for analysis of the lines, with an objective of 64 cm focal length, and 7 cm effective aperture. For photographing, Sakura film most sensitive to 9500 Å was used. The spectrograms for hydrogen and deuterium were nearly the same; the dispersion being about 100/Åmm, the wave-length could be detd. to 2 Å, referred to Ne-lines. To this limit, there is coincidence between the observed values for hydrogen and deuterium with those obtained by calcn. For more exact evaluation, grating spectrum should be used. It requires exposure of several hrs., while the prismatic spectrum was obtained in 90 min. giving members from $m=6$ to 17 extending from 10938 Å to 8467 Å for H. Poetker photographed $m=6$ to 11 in 40 hrs. with concave grating. Photo-

metric curve of the spectrogram for deuterium is shown in the figure. Owing to difference in photographic sensitivity, strong line $m=6$ is not prominent; the oxygen lines due to contamination are relatively strong. The oxygen line 84467 between $m=17$ and 18 is also present in the stellar spectra. Many minor lines belong to the secondary spectrum of deuterium, which is to be studied with higher dispersion. At the same time, the difference in wave-lengths between hydrogen and deuterium lines can be examd., being greater in the Paschen series than in the Balmer for the same member.

Authors.

An investigation of the pair creation by gamma rays in a cloud chamber.

M. Miwa and S. Kozima. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 757-765 (1937).—The production of pos. and neg. electron pairs in a lead target by the gamma rays of Th C'' was studied by means of a cloud chamber placed in the magnetic field. The energies of both partners of the pairs were detd. from the curvature of tracks, the total number of pairs being 151. The most of pairs were found to have the total kinetic energy of about 1.51 ± 0.02 mev. By making necessary corrections, the value was shown to be very close to the theoretical one $2.62 - 2 m_0 c^2 = 1.60$ mev. The partition of the energy between the individual partners of pairs was also studied and it was found that positrons had on an average a larger kinetic energy than electrons, as predicted by the theory of Jaeger and Hulme. But the difference of average energies of both partners seemed to be somewhat less than the value given by the theory. The energy of single positrons was also considered. Such an abrupt fall in the upper limit of energy distribution as reported by Alichanow and others, however, was never found.

Authors.

Energy distribution and behavior of mercury spectrum at high vapor pressure. T. Harada and T. Azuma. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 677-692 (1937).—On the commercial type quartz capillary mercury lamp at 30~40 atm, of

mercury vapor pressure, the relative energy distribution is studied between 2400 and 17000 Å. At these high vapor pressures the lines in the ultra-violet region decrease in intensity generally. The strongest line is 5461 and about 2/3 of the luminosity of the line spectrum is due to it in these lamps. The spectrograms of the quartz capillary mercury lamps specially constructed are taken between 2300 and 11000 Å and up to 100 atm. of mercury vapor pressure. All the arc lines with a few exceptions shift and broaden asymmetrically to the long wave length side. The width of the broadest lines (10140, 2537) are about 150 Å at 100 atm. The lines of which the initial terms are about 9.5 volt or higher than those in the normal state disappear in the continuous background at 100 atm. All the lines which remain relatively sharp up to about 30 atm. or at higher vapor pressures, belong to the sharp series. Between about 4000 and 5400 Å there appear some diffuse emission bands.

Authors.

Note on the calculation of spin-orbit interactions. T. Yamanouchi. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 161-165 (1937).—For the case that the term sepns. due to the spin-orbit interactions are small compared with the differences $E_n - E_{n'}$ of the energies of the unperturbed terms, a method is given for finding E_n from the observed data by the second order perturbation, and is illustrated by dp configuration of Sc II and V IV.

Author.

Energy of the configuration d^2p in intermediate coupling. T. Yamanouchi. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 166-171 (1937).—The energy matrices of d^2p configuration in L-S scheme are given by Condon-Shortley and Johnson, which contain 6 parameters arising from the Coulomb- and exchange-forces and the spin-orbit interactions. In this paper a method is described for finding these parameter values from the observed data. For $J=0, \dots, 4$, we get 5 equations by equating the diagonal sum of each matrix

to the sum of observed terms, and thus eliminate 5 parameters. The remaining one x is detd. by the theorem of the spectroscopic stability, according to which the sum of squares of the matrix elements is invariant under the unitary transformation. In this way, we get 3 quadratic equations, from which, as is shown by the examples, nearly coincident root is obtained. Other parameters are detd. from x , and it is shown that for corresponding ions the quantities arising from the electrostatic interactions are of the same order, while those arising from the spin-orbit interactions are much larger for the heavier elements. The calcn. is carried out for the isoelectronic sequences from Cu II to Ge V, and from Pd I to Te VII.

Author.

On the relation between the configuration of metallic complex salts and their absorption spectra. H. Sueda.

Bull. Chem. Soc. Japan, **12**, 188-198 (1937).

—From the comparison of absorption curves given by nitro-ammine-cobaltic complex salts near $360 m\mu$ of wave length, the following assumption was deduced: the absorption band presented by complex salt sols. can be resolved into the elements which are due to the pairs of co-ordinated groups situated in trans-position in a complex radical, and these elements show an additive property in the same complex ion. By taking into account the above-mentioned point of view, $K[Co(NH_3)_2(NO_2)_4]$ (Erdmann's salt) should have a trans-configuration. This assumption may also be applied to the absorptions given by aquo-chloro-ammine salts of cobalt and chromium in visible and ultra-violet regions.

Author.

The relation between the magnetic moment of a metal atom and its catalytic activity. T. Kitagawa. *This Journal*, **11**, 71-75 (1937).

The photographic action of sputtered platinum films. S. Ono. *This Journal*, **11**, 76-81 (1937).

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

Cryoscopic studies on the transition points of the compounds of organic solvents with salts. III. The congruent melting points of some alcoholates of alkali halides. H. Oosaka. *Bull. Chem. Soc. Japan*, 12, 177-187 (1937).—The lowering of the congruent melting points of the alcoholates— $\text{LiCl} \cdot 3\text{C}_2\text{H}_5\text{OH}$, $\text{LiCl} \cdot 4\text{C}_2\text{H}_5\text{OH}$, $\text{LiBr} \cdot 4\text{C}_2\text{H}_5\text{OH}$, and $\text{LiBr} \cdot 4n\text{-C}_3\text{H}_7\text{OH}$ —by the addn. of foreign substances were measured and the molecular depressions referred to 100 g of each alcohol were detd. From these cryoscopic consts. the heats of fusion of the alcoholates were calcd. When homologues of the solvent alcohol were used as solutes, abnormally low values were obtained for the cryoscopic const. This discrepancy may be considered to be due to the formation of a solid soln. between the alcoholate and the solute alcohol. This fact was verified semi-quantitatively. J. C. L.

On the anomalous change by heat-treatment of the electric conductivity of thin films of potassium chloride and sulphur. H. Saegusa and T. Matsumoto. *Sci. Repts. Tohoku Imp. Univ.*, I, 26, 159-166 (1937).—The electric conductivity of evaporated films of KCl and sulphur about 10^{-4}cm in thickness was studied. It was found that the variation of the electric conductivity with the temp. of a fresh film of KCl nearly satisfied the formula $\log \sigma = B + A/T$, and that after the heat-treatment the electric conductivity satisfied extremely well the above equation, and that its magnitude decreased to about one-tenth or one-hundredth of that of the fresh film due to the recrystallization. The magnitude of the change of the electric conductivity due to the heat-treatment of the film became larger as the temp. of the heat-treatment rose. In the case of a sulphur film, the change of the electric conductivity due to the heat-treatment was somewhat different, and it was not so distinct as that of the KCl film. Authors.

On the reduction equilibrium of cobaltous chloride by hydrogen. K. Sano. *J. Chem. Soc. Japan*, 58, 370-375 (1937).—The equil. consts. of the reduction of cobaltous chloride were measured statically at $759^\circ \sim 831^\circ\text{K}$ by using the palladium semipermeable membrane, and from the results obtained some thermodynamical values were calcd.

Author.

On the thermodynamical values of nickelous chloride. K. Sano. *J. Chem. Soc. Japan*, 58, 376-378 (1937).—The equil. consts. of the reduction of nickelous chloride by hydrogen were measured at $661^\circ \sim 792^\circ\text{K}$. The results obtained were in close agreement with those detd. by K. Jellinek and Uloth, Berger and Crut. Therefore, from the mean value of these three results, some thermodynamical values were calcd. Author.

Equivalent conductivity of the mixed solution of electrolytes. S. Kaneko. *J. Chem. Soc. Japan*, 58, 675-680 (1937).—The author extended Onsager-Fuoss' theory of the equiv. conductivity of mixed electrolytes, obtained a formula when ions have finite sizes, and applied his theory to the soln. of mixt. of HCl and KCl. Author.

The electrolytic formation of per-sulphate. III. The study of the electrodes. R. Matsuda and T. Nishimori. *Bull. Chem. Soc. Japan*, 12, 331-335 (1937).—The length of the Pt wire cathode is varied in the electrolysis of 15 N H_2SO_4 , and it is shown that the longer the cathode, the more the peroxidic products of the anodic reaction are reduced in spite of the smaller cathodic C. D. A PbO_2 anode which is prepd. by depositing PbO_2 electrolytically on a Pt wire anode gives a poor anodic current efficiency, the best value being only 3%. Gas carbon is tested as the anode material in electrolysing 10 N H_2SO_4 , 6 N $(\text{NH}_4)_2\text{SO}_4$ soln. and the latter one contg. ammonia, but the carbon is partly

disintegrated, in each case, during electrolysis. Various means are tested for the purpose of heating the Pt anode before its use and their effects on current efficiency are compared. Among the flames of three combustible gases, i.e., acetylene, coal gas and hydrogen, that of the first-named which is the richest in carbon or its compds. gives the greatest current efficiency and that of hydrogen the smallest. Alternating current is superior to direct one in the same respect as above, when applied to preheat the anode. Authors.

Researches on the electrolytic reduction potentials of organic compounds.

24. Consideration of the electrolytic reduction potential. I. Tachi. *Bull. Agr. Chem. Soc. Japan*, 13, 692-697 (1937).—According to J. Heyrovsky's theory, $\pi_{\frac{1}{2}}$ -potentials of diacetyl, acetophenone, benzoyl-acetone benzil, benzoin and azobenzene were detd. by the half wave method. The $\pi_{\frac{1}{2}}$ -potentials showed satisfactory constancy with the changes of the concn. of reducible compd. and of the sensibility of the galvanometer used with the given electrolytic soln. and temp. Then the $\pi_{\frac{1}{2}}$ -potential of org. compd. can take as the standard electrolytic reduction potential like the normal redox-potential of org. compd. $\pi_{\frac{1}{2}}$ -pH curves of benzoylacetone and azobenzene were plotted.

25. Standard Electrolytic reduction potential and redox-potential. *ibid.*, 698-704.—The electrolytic reduction of neutral red was investigated by the polarographic method. The half wave potentials ($\pi_{\frac{1}{2}}$) of neutral red in a given pH soln. showed a const. value, independent of the change of the concn. and of the sensibility of the galvanometer used. Then the $\pi_{\frac{1}{2}}$ -potential may be taken as a standard electrolytic reduction potential of neutral red. The standard electrolytic reduction potential (referred to normal hydrogen electrode) agreed with the redox-potential. The number of hydrogen atoms related to the electrolytic reduction of neutral red were detd. from the shift of the reduction potentials detd. by the tangent method and were assumed to be 2 atoms. The reduction

potential -pH curves are given in the original paper. Author.

Equivalent conductivity of 2-2 salts.

S. Kaneko. *J. Chem. Soc. Japan*, 58, 608 (1937).—From the theory already reported [*loc. cit.* 56, 1320 (1935).] a formula for equiv. conductivity of 2-2 salts is deduced and applied to the soln. of MgSO_4 . Author.

Theory of the activity coefficient in concentrated aqueous solution of strong electrolyte.

M. Abe. *Sci. Papers Inst. Phys. Chem. Research*, 16, 370-382 (1937).—The Virial equation on attraction was obtained on the basis of the Debye-Hückel theory of ion, and it was deduced for repulsion by accepting the Lorentz theory on gas as applicable to electrolytic soln. The following equations of osmotic pressure were obtained for the strong electrolytes which dissociate according to $A_{12} = v_1 z_1^{-1} + v_2 z_2^{-1}$ (z_1 and z_2 are valencies of ions).

$$\left[P + \sum_i \frac{a_i}{V} \frac{\beta_i}{V^{\frac{1}{2}} + \beta_i a_i} \right] \frac{V}{1 + \varphi/V} = v N k T, v = v_1 + v_2,$$

$$\alpha = \frac{N \epsilon^2 v_1 z_1^2}{6 D}, \quad \beta = \left[\frac{4 \pi N \epsilon^2 \sum_i v_i z_i^2}{D k T} \right]^{\frac{1}{2}}, \quad (i=1, 2),$$

$$\varphi = \frac{2}{3} \frac{\pi N (\delta_1^3 v_1^2 + \delta_2^3 v_2^2 + 2 \delta_1^2 \delta_2 v_1 v_2)}{v_1 + v_2},$$

$$\left(\delta = \frac{1}{2} (\delta_1 + \delta_2) \right),$$

where P denotes osmotic pressure, N Avogadro const., k Boltzmann const., ϵ electric quantity of electron, D dielectric const. of solvent, δ_1 and δ_2 diameter of ion. The relation between osmotic pressure of solute and both free energy and activity coeff. was considered thermodynamically, and the following equations were deduced to show the activity coeffs. of strong electrolytes.

$$\log f = - \sum_i \left[\frac{\epsilon^2}{3 D k T} \cdot \frac{v_i z_i^2}{v_i} \log (1 + \beta' \sqrt{C}) \right.$$

$$\left. + \frac{\epsilon^2}{2.303 \times 6 D k T} \frac{v_i z_i^2}{v_i} \frac{\beta' \sqrt{C}}{1 + \beta' \sqrt{C}} \right] + \frac{2}{2.303} \varphi c$$

$$\beta' = \frac{a_i \beta}{1 C^{\frac{1}{2} z_i^2}} = a_i \left[\frac{4 \pi N \epsilon^2}{10^8 D k T} \sum_i v_i z_i^2 \right]^{\frac{1}{2}},$$

where a_i denotes the quantity correlated with dimension of ion. If the quantity of pos. ion

and that of neg. ion are equal, $a_1 = a_2 = a$ is assumed. And the following equation is obtained.

$$\log f = -\frac{\varepsilon^2}{3DkTa} \frac{\sum v_i z_i^2}{v} \log (1 + \beta^1 \sqrt{C})$$

$$-\frac{\varepsilon^2}{2.303 \times 6DkTa} \frac{\sum v_i z_i^2}{v} \frac{\beta^1 \sqrt{C}}{1 + \beta^1 \sqrt{C}}$$

$$+ \frac{2}{2.303} \varphi C$$

J. C. L.

Chemical reaction in the silent electric discharge. XVI. Reaction between hydrogen and solid inorganic compounds. S. Miyamoto. *Bull. Chem. Soc. Japan*, 12, 313-315 (1937).—Studies on the reduction of a number of solid inorg. substances by hydrogen under the silent electric discharge were carried out. There follows an account of the results: (1) $2K_2CrO_4 + 3H_2 = 4KOH + Cr_2O_3 + H_2O$, (2) $K_2Cr_2O_7 + 3H_2 = 2KOH + Cr_2O_3 + 2H_2O$, (3) $2(NH_4)_2CrO_4 + 3H_2 = 4NH_3 + Cr_2O_3 + 5H_2O$, (4) $(NH_4)_2Cr_2O_7 + 3H_2 = 2NH_3 + Cr_2O_3 + 4H_2O$, (5) $Ca(ClO_3)_2 + 6H_2 = CaCl_2 + 6H_2O$, (6) $NaClO_3 + 3H_2 = NaCl + 3H_2O$, (7) $BaSO_3 + 3H_2 = BaS + 3H_2O$, $BaS + 2H_2O = Ba(OH)_2 + H_2S$, $BaS + H_2 = BaH_2S$, (8) $Th(NO_3)_4 + 16H_2 = Th(OH)_4 + 4NH_3 + 8H_2O$, $Th(NO_3)_4 + 4NH_3 + 4H_2O = 4NH_4NO_3 + Th(OH)_4$, $NH_4NO_3 + H_2 = NH_4NO_2 + H_2O$, (9) $(NH_4)_2S_2O_8 + 5H_2 = (NH_4)_2SO_4 + H_2S + 4H_2O$, $(NH_4)_2S_2O_8 + H_2 = (NH_4)_2SO_4 + H_2SO_4$, (10) $K_2S_2O_8 + 5H_2 = K_2SO_4 + H_2S + 4H_2O$, $K_2S_2O_8 + H_2 = K_2SO_4 + H_2SO_4$. J. C. L.

Measurement of specific heat of sodium carbonate by means of a twin calorimeter. M. Matui and S. Kitazato. *J. Soc. Chem. Ind. Japan*, 40, 555-558 (1937).—By making carbon tetrachloride a medium, specific heat of sodium carbonate was measured by means of a twin calorimeter. The result obtained is as follows: 0.2701 ± 0.00020 (20°).

J. C. L.

Effects of ultra-violet, X- and γ -rays on the electrical conductivities of solid insulators. S. Shimizu. *J. Electro-*

chem. Assoc. Japan, 5, 244-253 (1937).—(I) Ultra-violet rays. According to the study of B. Gudden and R. Pohl, it is a well-known fact that the electrical conductivities of dielectrics is affected by light. In this paper, the influence of ultra-violet rays on quartz and mica is examd., and its theoretical consideration studied. The following conclusions are reached. (1) The electric conductivities of quartz cut parallel and perpendicular to the C-axis are measured, under the influence of ultra-violet rays, and their numerical values are summarised. (2) The effect of ultra-violet rays on the conductivities of quartz cut perpendicular or parallel to the C-axis becomes small with an applied potential, and converges into a stationary value. (3) The similar phenomena of various micas exposed to ultra-violet rays are studied, and the value of $\left(\frac{\sigma_v}{\sigma}\right)_{t=3 \text{ min.}}$ varies from 27.6 to 2.0. (4) During the growth of polarization potential, the effect of ultra-violet rays is small, but if the applied potential is removed, it is large. (5) The mechanism of the influence of ultra-violet rays on the electrical conductivities of dielectrics is considered, and the energy to release one electron is also estimated. (II) X-rays. Without an applied potential, a residual current in dielectric crystals was measured, the latter being place in a dark room after they were exposed to X-rays. This phenomenon appears in quartz and calcite plates cut parallel to (100) plane, and rock-salts, artificial and natural (Stassfurt, Germany), cut parallel to (100), (110) and (111). The variation of the residual current with the time of exposure to X-rays, the effect of the thickness of specimen, the direction of X-rays and the residual current, the relation between the crystal surface and the direction of X-rays, the temp. effect, and the relation between the part exposed to X-rays and the rest of the crystal were studied. The action of X-rays upon a dielectric crystal is assumed to be similar to that of impurity in semi-conductors. (III) γ -rays. Residual current occurs in dielectrics by irradiation of γ -rays. These phenomena in paraffin, moonstone, quartz and ambloid were

studied. The direction of the current is equal to the case where the irradiated surface were brought to pos. electric potential. In piled specimens, the inner surfaces show neg. sign. The current increases with the irradiation time, and converges to a const. value. Author.

Studies on the membrane potential. J. Nakagawa. *Japan. J. Med. Biophys.* 4, 298-355 (1937).—I. The concn. effect of polyvalent cations upon collodion membranes. With very thin collodion membranes of graded permeability (the thinnest=ca. $1\ \mu$) it is found that the so-called "cation permeability" (L. Michaelis) is confirmed not only with univalent cations but also with polyvalent (Mg, Ca, Sr, Ba and La) as far as the solns. are dilute enough.—II. On the diffusion theory. The deviation in concd. soln. may be represented, assuming the diffusion theory of Nernst, by a simple approximate formula, $\frac{u}{v} = \frac{u_0}{v_0} \frac{c}{c+a}$, where u and v are the hypothetical mobilities within a membrane of cation and anion resp., and u_0 and v_0 those in the aqueous phase. a is a const. depending upon the permeability, i.e., the pore-size of a membrane and the valency of cation. The relative mobilities of univalent cations, at least, may be represented by the formula, $\frac{u'}{u''} = \left(\frac{u'_0}{u''_0}\right)^2$, where u'_0 and u''_0 are the mobilities in the free diffusion and β a const. depending chiefly upon the permeability. The decrease of u/v with increasing concn. would be due to the decrease of the magnitude of the neg. ζ -potential as the surrounding fluid is more concd.; the valency effect might be also ascribed to the reduction of the ζ -potential in the presence of polyvalent cation.—III. Amphoteric properties of the

membrane cong. neutral red. The collodion membrane cong. neutral red acts as an "anion permeable" membrane in an acidic medium. In an alkaline soln., on the contrary, it behaves as a "cation permeable" one. The reversal of the direction of the membrane potential would be caused by the change of the sign of the ζ -potential in an acidic fluid, in which dye-cation is dissociated and the membrane might be positively charged thereby. Author.

On the melting point and decomposition pressures of ammonium-carbamate at higher temperature. I. Kitawaki, S. Hori and M. Shimoda. *Repts. Tokyo Imp. Ind. Research Lab.*, 32, (6) 1-19 (1937).—By measuring the m.p. of ammonium-carbamate and its decompn. press. at 90° – 194.1°C ., the following results were obtained. (1) Ured formation is always recognized on heating ammonium-carbamate, and it is impossible to determine the true m.p. of ammonium-carbamate itself. The authors found that this point lies at temp. range 153.5° – 155.5°C . (2) The decompn. press. of ammonium-carbamate increased with temp. and was 57.7 atm. at 144.5°C . When the heating was continued further, the press. dropped suddenly and was 46.1 atm. at 145.0°C . A figure showing curves of decompn. press. and temps. is attached. Authors.

On the Becquerel effect of copper oxide electrode in alkali soln. N. Hayami. *This Journal*, 11, 166-188 (1937).

Thermal analysis of chemical reaction velocity. S. Horiba. *This Journal*, 11, 189-201 (1937).

4-COLLOID CHEMISTRY AND SURFACE CHEMISTRY

The lyophile property of celluloses. X. The electrokinetic phenomenon of various concentrations in the solutions of cellulose derivatives for the solvent.

K. Kanamaru and S. Kawano. *J. Soc. Chem. Ind. Japan*, 40, 187-191 (1937).—By making acetone soln. of the cellulose derivatives flow down into the solvent in electric field, the

flowing gradient for the direction of gravity was measured. The value of the boundary charge of ζ potential at the contact surface was obtained by varying the concn. of solns., and the meaning of the boundary potential was studied with respect to the phenomenon of solvation. J. C. L.

Electric boundary turbulence. XI. Absorption dispersion spectrum of electromagnetic wave of cellulose particle series at higher temperature. I. M. Shikata and S. Ueda. *J. Electrochem. Assoc. Japan*, 5, 93-105 (1937).—The absorption dispersion of electromagnetic wave (below 6,000 cycles and at the temp. range $30^{\circ}\sim 110^{\circ}\text{C}.$) at the lower region with respect to wood cellulose-liquid paraffin series was measured. The app. and the method used for the expt. were similar to those in the previous paper. The results obtained were as follows. (1) The wood cellulose-liquid paraffin series which did not show the dielectric loss at ordinary temp., when temp. was raised, began to produce the loss from the lower frequencies and electro-static capacity of the equiv. series was varied. When the number of frequencies was low, they showed a tendency to present the max. of the dielectric loss in the higher temp. region. (2) When the number of frequencies was equal, they began to produce the loss, as the temp. became higher, in the lower region contg. water and to show the variation of the electro-static capacity of the equiv. series. The max. of the dielectric loss appeared where water contained was const. (3) When the number of frequencies was varied, there appeared the max. point of the dielectric loss. The number of frequencies in which the max. point appeared migrated to the higher frequencies, as the quantity of water contained became greater and the temp. of measuring higher, and its max. value became great. As for the electrostatic capacity of equiv. series, Cs became smaller towards the region of higher temp. as the number of frequencies became higher. But in the range where the dielectric loss did not appear because of low temp. or little absorbed water, the higher the number

of frequencies became, the greater the increase in the electro-static capacity of equiv. series. (4) The greater the quantity of water contained and the higher the temp. measured, the less became the relaxation time τ . (5) The theoretical consideration for the results obtained is quite similar to that already reported in the previous paper. J. C. L.

Preparation of silica gel. H. Ando. *Rep's. Tokyo Imp. Ind. Research Lab.*, 31, (5) 77-156 (1937).—In preparing silica gel by mixing sodium silicate with an acid, the influence of the procedures upon the adsorption capacity and form of products were studied by examination of the materials, the manner of mixing, coagulation, contraction, washing, drying and heating. The conditions necessary to increase effectively adsorption capacity, intensity, and the size of silica gel were detd. J. C. L.

Adsorption of silica gel. H. Ando. *Rpts. Tokyo Imp. Ind. Research Lab.*, 31, (5) 1-75 (1937).—With respect to silica gels prepd. by different methods, adsorbability of gas and vapour of various liquids was measured by the static and the dynamic method, and the adsorbability was classified into adsorption intensity and adsorption capacity. It was found that the adsorbability is remarkably different according to the sort of silica gel; the adsorbed amt. at the smaller humidity range is dependent of the adsorption intensity which is characteristic to the sample and that at the greater humidity range is detd. by the adsorption capacity. When adsorption temp. and humidity are const., the adsorption capacity by the static method and that by the dynamic method are equal. Sp. gr. of silica gel was measured, and it was found that the const. relation of quantity is held between the sp. gr. and the adsorbed amt. of satd. vapour. The curve of adsorption of vapour is given. When the grain of silica gel is made small, its adsorption capacity and intensity are slightly decreased. The comparison of silica gel with active carbon and the theoretical consideration of its adsorption are stated. J. C. L.

Adsorption of solvent vapour by the solute crystal. I. Uhara and M. Nakamura. *Bull. Chem. Soc. Japan*, 12, 227-233 (1937).—Lumping of powd. of soluble solid substances in the wet air at common temp. is observed even when the humidity or vapour pressure of water is lower than that of the satd. soln. of the substances, and this phenomenon is not attributed to mere deliquescence. Both adsorptions of water vapour by powd. and surface conductance of crystal of KBr increase with humidity of air, and this increase is very sharp as the humidity approaches that of the satd. soln. Accordingly, it is considered that adsorbed water on the soluble substances shows to some extent the function as the solvent; and ions or molecules of the crystal surface become mobile, and if the adsorption layer is of some thickness a sort of soln. is formed, of which vapour pressure is lower than that of the satd. soln. Lumping of powd., surface conductance and electrolysis and increased velocity of reactions between solid substances are explained by these considerations in cases of soluble substances.

Authors.

Studies on the sorption of gases by titania gel. IV. The sorption of water vapour and the capillary condensation as a part of the sorption phenomenon. I. Higuti. *Bull. Inst. Phys. Chem. Research*, 16, 536-547 (1937).—The effect of heating the gel in temp. range 52° ~ 1000°C was examd. by studying the isotherms at 20°C. The primary part of the isotherm, which is concave to the pressure axis and considered to be due to van der Waals' adsorption, was lowered very rapidly with the heating temp. of the gel and almost disappeared by heating the gel at 800°C for 90 minutes. However, the succeeding secondary part still survived even in the case where the gel was dehydrate to a great extent and the fine particles seemed to become more crystalline. Considering these results combined with those previously obtained the author has concluded that the secondary part may be due to capillary condensation and that the dimen-

sions of pore radius several times larger than the molecular dimensions of the sorptive is large enough to cause capillary condensation. The sorption, desorption and resorption etc. were measured at 20° and 30°C with the same gel as that used in the previous expts. The capillary condensation theory may explain the facts that the relation between the liquid volume of condensed water and the capillary pore radius is independent of temp. and that the differential heat of sorption is const. and near the heat of condensation. Finally it was shown that McBain's suggestion for the mechanism of hysteresis in hydration (1935) might be extended to the general explanation of hysteresis in the sorption phenomena of vapours by porous sorbents.

Author.

Surface tension of heavy water. T. Takéuchi, T. Sugita and T. Inai. *Proc. Phys.-Math. Soc. Japan*, III, 19, 552-554 (1937).—Using a capillary U-tube of radii $\frac{1}{1.578}$ mm and $\frac{1}{0.30902}$ mm and of length 1.6 cm placed in a thermostat, surface tension of heavy water γ (dyne/cm) at some temps. are measured by reading the positions of two surfaces in the tube with a microscope. The tube const. $\frac{g}{2} \left(\frac{1}{r} - \frac{1}{R} \right)^{-1}$, where r and R are the radii of two bores and g the acceleration of gravity, is detd. in two ways, by the observation of surface tension of ordinary water and by direct calcn., and is found to be 38.334 C.G.S. Density of heavy water ρ gm/cm³ is expressed in two empirical formulas obtained by the method of least square:

$$\rho = 1.1065 + 10^{-4}(-14.3 + 2.4711 t - 0.11142 t^2 + 0.0001030 t^3 + 0.00005459 t^4)$$

for $t = 0^\circ \sim 60^\circ$,

$$\rho = 1.1065 + 10^{-4}(96.30 - 3.6945 t - 0.01355 t^2)$$

for $t = 40^\circ \sim 100^\circ$,

the values being taken from Perperot-Schacherl's paper. But formula analogous to Thiesen's for ordinary water can not be obtained. Eötvös' formula for heavy water is obtained as follows:

$$\frac{\gamma}{\rho^{\frac{2}{3}}} = -0.1405097 (t - 502.3476),$$

critical temp. being higher than that for ordinary water.

Authors.

On the rigidity and the constitution of thermoreversible gel. F. Hirata. This Journal, 11, 107-119 (1937).

On the chemisorption of carbon dioxide by reduced iron. I. K. Kawakita. This Journal, 11, 39-53 (1937).

A study of the energy distribution of the active centres of catalysts by the adsorption of poisonous substances. I. The decomposition of hydrogen peroxide with platinum black poisoned by mercuric ion. M. Kubokawa. This Journal, 11, 202-216 (1937).